SPECTROSCOPIC STUDIES OF THE VAPORIZATION OF REFRACTORY MATERIALS

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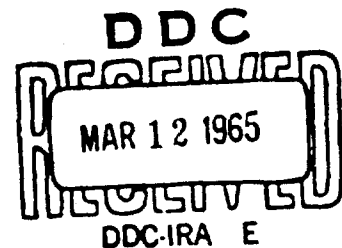
I. STATUS AND SUMMARY

During the elapsed third quarter, matrix isolation and resonance line absorption studies have been continuing.

Matrix isolation spectra in solid argon have been obtained on 10^{18} enriched ThO_2. From the resulting spectra it appears that the molecule is highly bent. Frequencies have been assigned to the ν_1 and ν_3 vibrational fundamentals for all the various isotopic species. ν_2 was not observed in the frequency region (2 μ to 55.5μ) covered and must be presumed to be less than 180 cm^{-1}.

Modifications of our spectroscopic equipment have been made and it is now possible to obtain infrared spectra down to 180 cm^{-1}. We have reexamined the long wavelength regions of the spectra of MgF_2 and AlF_3 using this modified equipment and have obtained additional spectra for lithium fluoride.

Resonance line studies have been initiated on ZrN in a manner completely analogous to that used in the TiN study. However, much difficulty was encountered because of the reaction of the ZrN with carbon. Modifications of the furnace are being made to try to mitigate this reaction.

Two papers were presented at the Ohio State Symposium on Molecular Structure and Spectra on the magnesium halide work and our previously completed work on Al_2O. The Al_2O study has recently appeared in the Journal of Chemical Physics $\left[\text{J. Chem. Phys. } \underline{41}, 542 \ (1964) \right]$.

II. TECHNICAL STATUS - EXPERIMENTAL RESULTS AND DISCUSSION

A. MATRIX ISOLATION

The long wavelength capability of our instrumentation has been extended to around 55.5 microns (180 cm^{-1}). This has been accomplished through the modification of the model 12 grating instrument by replacing the grating with one blazed for the 45 μ region and by using various filter and restrallen plate combinations. We are apparently limited by the cesium iodide windows in the dewer and hope to increase the wavelength coverage to approximately 60 μ through the use of polyethylene windows. The spectral resolution has also correspondingly been improved by use of the grating instrument. We have used this modified instrumentation to reexamine the long wavelength region of the spectra of MgF_2 and AlF_3. The heretofore, unobserved Blu mode of the Li_2F_2 has also been seen using this modified instrumentation. In this case a 50-50 mixture of Li^6F and Li^7F was vaporized and a triplet in solid argon was observed at 293.8 cm^{-1}, 285.6 cm^{-1} and 277.3 cm^{-1}. This triplet has been assigned to the molecular species $Li_2^6F_2$, $Li^6Li^7F_2$ and $Li_2^7F_2$ respectively, and represents the Blu out of plane funda-mental for the dimer molecule. The isotope frequency ratio agrees exactly with the predicted value for this mode. Two frequencies at 265.4 cm^{-1} and 260.3 cm^{-1} have also been observed and we feel that these frequencies along with the isotopic pairs previously observed at 518 cm^{-1} and 497 cm^{-1} and at 769 cm^{-1} and 722 cm^{-1} belong to a triatomic species containing one lithium atom (e.g. LiF_2^-). Such a species may possibly be formed in the matrix. There is no indication of charged particles in the effusing beam.

Magnesium and Aluminum Fluorides

As mentioned above the long wavelength regions of the spectra of MgF_2 and AlF_2 have been reexamined with our modified instrumentation. In the case of MgF_2, the band previously reported at 247 cm^{-1} in solid argon when observed with the grating instrument, appears as a strong major band at 246.1 cm^{-1} with an indication of two side bands at 243.9 cm^{-1} and at ~ 240 cm^{-1}. (This last band, ~ 240 cm^{-1}, is very weak and may be spurious).

Three bands are to be expected if indeed we are observing the bending mode, ν_2, of MgF_2 since magnesium contains three naturally occuring isotopes, Mg^{24} (79%) Mg^{25} (10%) and Mg^{26} (11%). From the observed isotopic frequency shifts (~ 2 cm^{-1}) it must be concluded that MgF_2 is slightly bent since the observed shifts are smaller than the predicted value (~ 3 cm^{-1}) for a linear molecule. This conclusion is not inconsistent with our previous results, however, if the molecule is bent ν_1, the symmetric stretch should be active and one of the frequencies in the 400 cm^{-1} to 500 cm^{-1} region previously attributed to polymer may indeed be ν_1. More refined calculations using these newly observed frequencies are under way.

In the case of AlF_3, the long wavelength region of the spectrum was also reexamined using the grating instrumentation. The results in solid argon are identical to the previous results obtained with the prism instrument. In the case of the solid krypton matrix, the previously observed feature at 245 cm^{-1} (using the prism instrument) appears as two features, one at 244 cm^{-1} and the other at 242 cm^{-1}. This observation helps to make the data more self consistent since previously three features were observed in solid argon whereas only a single long wavelength feature was seen in solid krypton. Now it appears that the three features in argon go over to two features in krypton. It is altogether possible that the krypton matrix does not remove the degeneracy of the ν_4 (E') mode as effectively as solid argon and therefore only two frequencies are evident in the long wavelength region (ν_2 and ν_4).

Thoria

A sample of O^{18} enriched ThO_2 was obtained from the Volk Radiochemical Company and had an enrichment of approximately 45%. The material was loaded into a standard tungsten Knudsen cell and degassed in the usual fashion. Degassing of the sample proved to be a long and arduous task since the material was contaminated with a large amount of ammonium chloride. The spectrum of this isotopically enriched sample was obtained in solid argon in the region 2 μ to 55.5 μ and a typical spectrum and conditions are given in Figure 1.

In a previous report, the infrared spectrum of ThO_2^{16} was given.[1] From a comparison of Figure 1 with the O^{16} spectrum, the identification of those features belonging to the various isotopic molecular species is obvious. The spectrum consists of two triplets and a doublet; the triplets being due to the ThO_2 species ThO_2^{16}, $ThO^{16}O^{18}$, and ThO_2^{18} while the doublet is due to the ThO species ThO^{16} and ThO^{18}. The relative intensities of observed features are consistent with the isotopic enrichment of the sample. The triplet, 734.5 cm^{-1}, 707.7 cm^{-1} and 695.9 cm^{-1}, due to the species ThO_2^{16}, $ThO^{16}O^{18}$ and ThO_2^{18} respectively constitutes the most intense feature of the observed spectrum and must be assigned to ν_3 the asymmetric stretch. From the values 734.5 cm^{-1} and 695.9 cm^{-1} an estimate of the apex angle can be made. This results in a value for the apex angle around $106°$. It should be pointed out that because of the massiveness of the central thorium atom in ThO_2, the calculation of the apex angle from the isotopic frequencies is not very sensitive. Nevertheless, it is felt that this result indicates strongly that the ThO_2 molecule is highly bent. In view of this result, it becomes quite plausible to assign the other triplet (786.8 cm^{-1}, 773.4 cm^{-1} and 743.8 cm^{-1}) to ν_1 the symmetric stretching mode. Since for molecules which are highly bent it is not unusual to have ν_1 occur at higher frequencies than ν_3.[2] The doublet, $877.6 - 880.3$ cm^{-1} and 830.9 and 833.3 cm^{-1}, the higher member of which was previously proven to be due to ThO^{16}, yields and isotope frequency ratio in exact agreement with the predicted value for ThO.

From the above assigned isotopic frequencies for ν_3 and ν_1 of ThO_2 and using an apex angle of $106°$, it is possible to estimate ν_2 the bending frequency. This has been done using a three term potential function,[3] and yields the following results:

$$\nu_2(ThO_2^{16}) \quad = \quad 124 \text{ cm}^{-1}$$

$$K_1 \quad = \quad 5.11 \times 10^5 \text{ dynes/cm}$$

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$$\frac{K_8}{\ell^2} = .067 \times 10^5 \text{ dynes/cm}$$

$$K_{12} = .44 \times 10^5 \text{ dynes/cm}$$

Again it should be pointed out that the massiveness of the central thorium atom makes this type of calculation quite insensitive. Further refinements in these calculations will be attempted in the near future. Experimentally it is known that the bending mode ν_2 lies below 180 cm^{-1} and therefore, some validity should be attached to the above calculated values.

Resonance Line Absorption Studies

A sample of ZrN was obtained from the Metal Hydrides Company. This material was used in the resonance line absorption set up in a manner completely analogous to the technique used in the TiN study.[4] However, no consistent results could be obtained. It was found that the apparent vapor pressure of zirconium kept changing with the time of heating, the sample being held in an ambient environment of nitrogen. It was finally concluded that at the temperature at which a sufficient intensity of absorption of the zirconium atoms could be produced that the vapor pressure of carbon was sufficiently high to react rapidly with the ZrN sample and form ZrC. This was further confirmed by X-ray diffraction analysis of the heated sample and by noting that the vapor pressure of the zirconium was approaching that of ZrC. We are presently attempting to isolate the nitride from the carbon by using a molybdenum tube as a liner inside the graphite furnace.

III. FUTURE WORK

Matrix isolation studies will be started on ZrO_2.

Resonance line studies will continue on ZrN.

REFERENCES

1. G. M. Kibler, T. F. Lyon, M. J. Linevsky and V. J. DeSantis, WADD TR 60-646 Part IV, January 1964.

2. D. E. Mann, Private Communication.

3. G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, 1945.
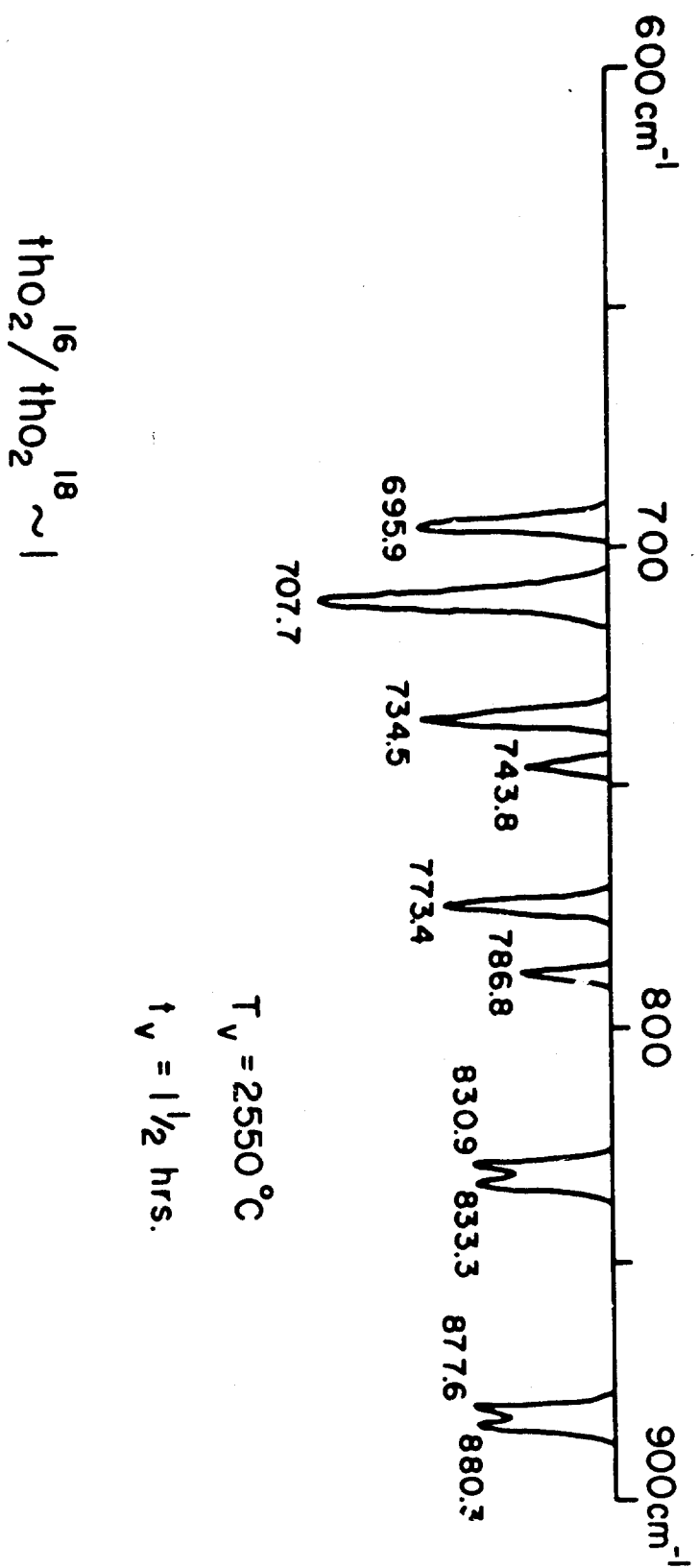
Figure 1. Infrared Spectrum of ThO$_2^{16}$ - ThO$_2^{18}$ in Solid Argon.

ThO$_2^{16}$/ThO$_2^{18}$ ~ 1

T_v = 2550 °C

t_v = 1 1/2 hrs.

600 cm^{-1}

700

800

900 cm^{-1}

695.9

707.7

734.5

743.8

773.4

786.8

830.9

833.3

877.6

880.7